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Carbon-13 Nuclear Magnetic Resonance of Phenolic Resins. Positional Isomers of Bis(hydroxybenzyl)phenols and Bis(hydroxyphenyl)methanes[1]

Stanley A. Sojka,*‡ Roger A. Wolfe,‡ Edward A. Dietz, Jr.,‡ and Bobby F. Dannels*

Hooker Chemical and Plastics Corporation, Research Center and Durez Division, Grand Island Complex, Niagara Falls, New York 14302. *Received March 28, 1979*

ABSTRACT: The ^{13}C NMR chemical shifts of positional isomers of bis(hydroxybenzyl) phenols and bis(hydroxyphenyl) methanes are reported. The ^{13}C NMR chemical shifts of these oligomers are assigned and grouped into classes. These data are useful for the understanding of more complex resin systems.

We wish to report the ^{13}C NMR chemical shifts of all seven possible positional isomers of bis(hydroxybenzyl)-phenols and the three positional isomers of bis(hydroxyphenyl)methanes. The study of these small oligomers is necessary for the complete understanding of more complex phenolic resin systems. Recent interest in the utilization of ^{13}C NMR spectroscopy to study the structure and composition of phenolic resins has prompted us to disclose some of our initial results.[2-6]

A low molecular weight phenolic resin was made by dropwise addition of 600 g (7.4 mol) of 37% aqueous formaldehyde into 3500 g (37.2 mol) of phenol and 17 g (0.2 mol) of oxalic acid at 100 °C. The temperature was maintained at 100–110 °C for 1 h after the addition. The reaction mixture was vacuum distilled and a fraction of bis(hydroxybenzyl)phenols (12 g) was collected (bath temperature was 340–360 °C (0.02–0.03 mm)). Purified bis(hydroxybenzyl)phenol isomers were obtained by separating this fraction by LC using a E.S. Industries Chromegaprep™ bonded diol column (50 cm × 9.6 mm i.d.). A 2% $CH_3OH/CHCl_3$ (vv) elution solvent was used at a flow of 5.5 mL/min. Component detection was at 254 nm. Purified bis(hydroxyphenyl)methane isomers were obtained by column chromatography of an isomeric mixture (Bisphenol F, Rhodia, Inc., Chemicals Division) on silica gel (Baker, 60/200 chromatographic grade) using 1.5% $CH_3OH/CHCl_3$ (vv) as elution solvent. The purity of isomers was found to be >90% in all cases by reinjection on the chromatographic column.

Carbon-13 chemical shifts were measured at ambient temperature using a Varian XL-100 spectrometer equipped with a Nicolet TT-100 pulse apparatus. Quadrature phase detection was used, and free induction decays were collected over 8K points. The time between 30° pulses was 25 s, and the number of scans varied between 1000 and 4000. Gated decoupling was used to suppress the Nuclear Overhauser effect. Samples were ~5% in THF-d_8 which also served as an internal field-frequency lock signal and an internal chemical shift standard. The chemical shifts were converted to the Me_4Si scale using the relationship: $\delta(Me_4Si) = \delta THF\text{-}d_8 + 25.3$. The measurements of these materials in dilute solution will reduce solvent and concentration effects upon the chemical shifts.

The ^{13}C chemical shifts and assignments are compiled in Table I for phenol (**1**), 2,2′-bis(hydroxyphenyl)methane (**2**), 2,4′-bis(hydroxyphenyl)methane (**3**), 4,4′-bis(hydroxyphenyl)methane (**4**), and all the bis(hydroxybenzyl)phenol isomers **5**–**11**. Figure 1 shows the structures of isomers **5**–**11**. Assignments were based upon chemical shift analogy to methyl-substituted phenols, integrated peak areas, and internal consistency. In some cases, proton

‡ Research Center.
* Durez Division.

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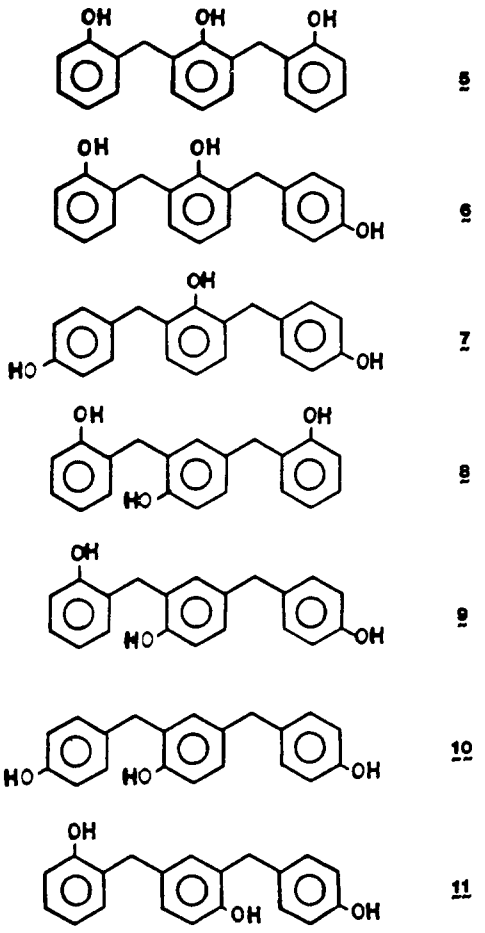


Figure 1. Structures of the seven possible positional isomers of bis(hydroxybenzyl)phenols.

coupled scans were recorded as an assignment aid. The spectrum of each isomer is unambiguous by virtue of its unique ^{13}C NMR spectrum (vide infra).

The bridging methylene carbons are separated according to their spatial relationship to hydroxyl as previously reported.[7] Thus, 2,2′-methylene carbons appear at ~31 ppm, 2,4′-methylene carbons at ~36 ppm, and 4,4′-methylene carbons at 41 ppm. These carbons apparently are influenced by an upfield γ substituent effect[8] of about 5 ppm per γ-hydroxyl. More subtle chemical shift influences are further evident for 2,2′- and 2,4′-methylene carbons. In the bis(hydroxybenzyl)phenols, each of these carbon types are divided into two groups according to the substitution pattern of the middle phenol ring. Those 2,2′-methylene carbons which are a part of a 2,4-disubstituted phenol ring resonate at 30.8–30.9 ppm, and those that are a part of a 2,6-disubstituted phenol ring appear at 31.3–31.4 ppm. Likewise, those 2,4′-methylene carbons which are a part of a 2,4-disubstituted phenol ring resonate at 35.5–35.7 ppm, and those that are a part of a 2,6-disubstituted phenol ring resonate at 35.9 ppm. Interestingly, the 2,4′-methylene carbons of isomer 11 exhibit slightly different chemical shifts, indicating a small but measurable effect of chemical environments. Finally, the 4,4′-methylene carbons appear only at 41.0 ppm because the middle ring must always be a 2,4-disubstituted phenol ring.

The phenoxy carbon region of the ^{13}C NMR spectrum is the most interesting from an analytical standpoint. This region yields such important information as the amount of free phenol present, the concentration and kinds of end groups (monoalkylated phenols) and middle groups (dialkylated phenols), and the concentration of branching

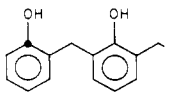
Table I
Carbon-13 Chemical Shifts for Phenolic Resin Oligomers[a]

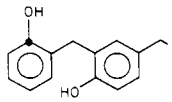
compd no.	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-1″	C-2″	C-3″	C-4″	C-5″	C-6″	2,2′-	2,4′-	4,4′-
1	158.7	116.0	130.1	119.9	130.1	116.0															
2	155.6	128.4	131.5	120.7	128.1	116.0													30.9		
3	156.0	129.5	131.2	120.3	127.8	115.6	155.6	128.4	131.5	120.7	128.1	116.0								35.6	
4	156.5	116.0	130.6	133.8	130.6	116.0	156.5	115.8	130.7	132.9	130.7	115.8									41.0
5	155.2	128.4	131.4	120.8	128.0	115.7	153.1	128.6	129.3	120.8	129.3	128.6	155.2	128.4	131.4	120.8	128.0	115.7	31.3		
6	154.8	128.4	131.3	120.9	127.9	115.6	153.4	130.0	129.0	120.3	129.0	128.2	156.7	115.7	130.6	132.5	130.6	115.7	31.4	35.9	
7	156.8	115.8	130.5	132.1	130.5	115.8	153.5	129.4	128.9	120.4	128.9	129.4	156.8	115.8	130.5	132.1	130.5	115.8		35.9	
8	155.7	128.6	131.1	120.3	128.4	115.8	153.7	127.8	132.2	133.2	127.4	115.6	156.1	129.5	131.0	119.9	127.6	115.4	30.8	35.5	
9	155.7	128.6	131.1	120.3	128.2	115.8	153.8	128.0	131.9	133.9	127.6	115.8	156.8	115.8	130.3	133.4	130.3	115.8	30.8		41.0
10	156.6	115.6	130.5	132.9	130.5	115.6	154.2	129.1	131.7	133.5	127.9	115.5	156.7	115.8	130.3	133.5	130.3	115.8		35.7	41.0
11	156.1	129.6	130.9	119.9	128.1	115.4	154.1	128.9	132.0	132.7	127.4	115.4	156.6	115.6	130.4	133.0	130.4	115.6		35.7[b]	
																				35.5	

[a] The carbons are numbered with respect to the structures drawn in Figure 1. The phenol ring at the left used unprimed numbers, the middle ring used primed numbers, and the right ring used double primed numbers. Numbering of each ring starts with the phenoxy carbon and proceeds around the ring toward the site of nearest substitution. Methylene carbons are identified according to their spatial relationship to hydroxyl. [b] 2,4′-Methylene carbon at 35.5 ppm and 2′,4″-methylene carbon at 35.7 ppm.

Table II
Compilation of ^{13}C Chemical Shift Regions for Various Carbon Types Found in Phenolic Oligomers[a]

C-O


(154.8-155.2)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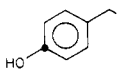
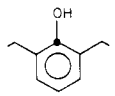
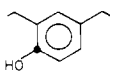
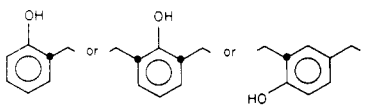
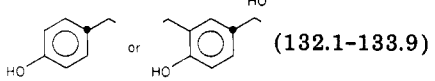

(156.5-156.8)


(153.1-153.5)

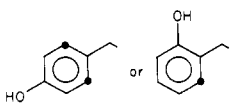

(153.7-154.2)

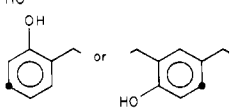
C-R

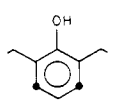

(127.6-130.0)

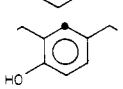

(132.1-133.9)

3-C, 5-C

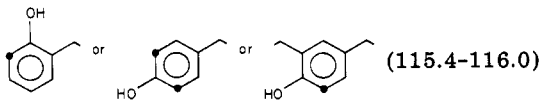

(130.3-131.5)


(127.4-128.4)

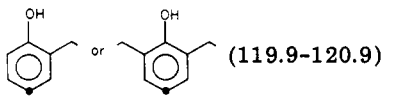

(128.9-129.3)


(131.7-132.2)

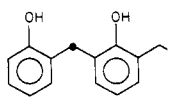
2-C

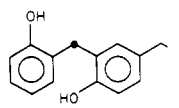

(115.4-116.0)

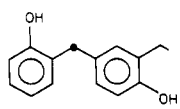
4-C

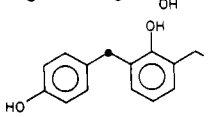

(119.9-120.9)

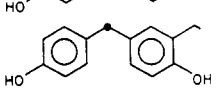
-CH_2-


(31.3-31.4)


(30.8-30.9)


(35.5-35.7)


(35.9)


(41.0)

[a] Numbers in parentheses are the ^{13}C chemical shift regions for the dotted carbons in the adjacent structure.

centers (trialkylated phenols) and allows for a calculation of an averaged molecular weight.[6] This abundant and intimate information is difficult or impossible to obtain by other methods.

The phenoxy carbon chemical shifts of the end phenol ring are divided into two groups according to the position of alkylation. Thus, the phenoxy carbon shifts for end phenol groups alkylated in the 2 position are between 154.8 and 156.1 ppm, while those alkylated in the 4 position are between 156.5 and 156.8 ppm. Furthermore, the phenoxy carbon chemical shifts of 2-alkylated phenolic end groups reflect the substitution pattern of the neighboring phenol ring. A 2,6-dialkylated middle phenol ring causes the phenoxy carbon of a 2-alkylated end phenol ring to appear between 154.8 and 155.2 ppm, whereas a 2,4-dialkylated middle phenol ring causes this carbon to appear between 155.7 and 156.1 ppm. Unfortunately, the phenoxy carbon chemical shifts of 4-alkylated phenolic end groups were not sensitive to the substitution pattern of the adjacent ring.

The phenoxy carbon chemical shifts of the middle phenol rings are divided into two groups according to the ring substitution pattern. The phenoxy carbon chemical shifts of 2,6-disubstituted phenol rings are between 153.1 and 153.5 ppm, whereas those which are 2,4-disubstituted are between 153.7 and 154.2 ppm. It is difficult to discern any meaningful influence the substitution pattern of the neighboring end groups has on these carbons with the present compounds.

The chemical shifts of alkylated aromatic carbons are predominantly determined by their proximity to hydroxyl. Surprisingly, this is true irrespective of whether the phenol ring is an end or middle group. Thus, those alkylated carbons in the 2 or 6 position relative to hydroxyl resonate between 127.6 and 130.0 ppm, while those in the 4 position resonate between 132.1 and 133.9 ppm. There are more subtle influences on the chemical shifts caused by the substitution pattern of the neighboring phenol ring, but additional work on larger oligomers is necessary before these can be adequately discerned.

The chemical shifts of the aromatic carbons in the 3,5 position overlap with those of the alkylated carbons causing interpretive complexity. However, some generalizations may be made. The chemical shifts of the 3,5-carbons may be grouped into classes according to the proximity of alkyl substitution. Thus, those 3,5-carbons in the 4-alkylated end phenol rings and those 3-carbons in 2-alkylated end phenol rings appear at 130.3–131.5 ppm.

Those 5-carbons in 2-alkylated end phenol rings and 2,4-disubstituted phenol rings appear at 127.4–128.4 ppm. Those 3,5-carbons in 2,6-disubstituted phenol rings are between 128.9 and 129.3 ppm, whereas 3-carbons in 2,4-disubstituted phenol rings are between 131.7 and 132.2 ppm.

All unsubstituted aromatic carbons in the 2 or the 6 position resonate in a very narrow spectral region, between 115.4 and 116.0 ppm. This was independent of the position of the phenol ring in the molecule and its substitution pattern. Likewise all unsubstituted aromatic carbons in the 4 position are between 119.9 and 120.9 ppm, irrespective of position of the phenol ring in the molecule.

The chemical shift trends noted above are tabulated in Table II for easy reference. With these results as background, the interpretation of more complex resin systems may be attempted with the view of obtaining very intimate structural and compositional detail. We intend to expand this data base by examining larger oligomers and by investigating the effects of ^{13}C chemical shifts caused by branching centers (trialkylated phenol rings).

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A New Theoretical Approach of the Secondary Nucleation at High Supercooling

J. J. Point

Service de Chimie Physique et de Thermodynamique, Université de l'Etat à Mons, 7000-MONS, Belgium.

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ABSTRACT: A new model for lamellar crystallization is presented. It ensures a finite crystal thickness at every supercooling. The result comes from a detailed description of the buildup of a secondary nucleus in which the segmental nature of the linear macromolecules is explicitly considered. The potentialities of the new model are illustrated by detailed calculations of the dependence of the lamellar thickness on the crystallization temperature and by considering the dependence of the crystal thickness of polyamides on the length of their repeating unit.

The dependence of the thickness of lamellar crystals, L, of polymers on the crystallization temperature, T_c, was the subject of numerous experimental and theoretical studies. In this paper, our main concern will be the overall shape of the L vs. T_c curves. It is well-known that the following general dependence of L on T_c is observed; it consists of an inverse dependence on the undercooling ΔT, at low ΔT values, tending to an invariant value beyond a certain ΔT. At low undercooling, the situation is known from the very beginning.[1] At high undercooling, the presence of the long horizontal plateau instead of an upswing in L is first observed for polyamides and polystyrene[2] and is now appreciated as generally valid.

Various suggestions were made in order to explain these experimental observations. One of these suggestions seems to be successful and leads to the well-known theory of Lauritzen and Hoffman.[3] These authors consider the effect of a physical adsorption on the surface, prior to actual crystallographic attachment onto the substrate. Such an hypothesis leads to a decrease in the driving force for the crystallization and to an increase in the critical undercooling, ΔT_c. The choice of the parameter ψ used to express the amount of the reduction of the driving force for the crystallization is critical. Decreasing ψ allowed the taking into account of a higher ΔT_c. A 0.382 value gives the best fit for the L vs. ΔT curve of the polystyrene at a supercooling as high as 190 °C. A 0.7 value gives the best fit for polyethylene at a supercooling as high as 80 °C. The choice of these ψ values is not clearly related to the chemical nature of the polymer. Lower values of ψ do not permit the avoidance of the δl catastrophe. Higher values lead to a continuous decrease in L with an increase in ΔT instead of the observed long plateau. In conclusion, it is not obvious that the Lauritzen–Hoffman theory, in this form, is the best explanation of a situation which, on experimental grounds, seems to be quite general. Therefore, we are searching for alternative explanations.

In the discussion of their results on polystyrene, Jones, Latham, Keller, and Girolamo[2a] questioned the steady state approximation, intrinsic of the usual derivation of the kinetic theory. But when the crystallization is rather slow, as in the case of polystyrene, departures from the steady state are considered as being of little significance (as noted by Jones[2a]). Moreover, it can be shown, on a theoretical basis, that the time constants involved are short and that the steady state approximation is readily usable. This particular point is to be discussed in a forthcoming paper with J. K. Platten.

A more complete discussion of the complexity of such a process as the attachment of a long fold stem of flexible molecular chain to the crystal seems to be another important point. The question was raised by Frank and Tosi[4] (see also Jones[2a]) a long time ago. Frank and Tosi established more clearly the distinction between two situations. In the first situation, a range of configurations, corresponding to the partial attachment of a stem, is considered as belonging to one stage. In the second situation, they assume that in the attachment process of a

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